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None hazardous chemical method for etching thin film silicon nitride using aqueous solutions of chelating agents

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Abstract

Structuring of thin film silicon nitride (SiN) is often done by etching the thin film using hydrofluoric acid (HF) or phosphorus acid, two hazardous chemicals. We present a non-hazardous method to structure thin film SiN using aqueous solutions of chelating agents at moderate temperatures to slowly etch thin film silicon nitride. Using solutions of citric acid as a model solution, we achieve etch rates of up to [3.14 ± 0.06] nm/h at 90°C for PECVD grown SiN. Experiments with aqueous solutions of tartaric acid show etch rates of at least [4.38 ± 0.02] nm/h at 80°C for PECVD grown SiN. The etching mechanism is determined as a partial hydrolysis of the SiN involving free H+ ions.

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Keywords: silicon nitride; chemical etching; LPCVD; hydrolysis; etching mechanism; thin film; chelating agents; non hazardous

1. Background and State of the Art

Structuring of thin film silicon nitride (SiN) is either done by etching using large machinery like DRIE [1] or by using hazardous chemicals like hydrofluoric acid (HF) [2] or phosphorus acid [3] at high temperatures. These etching processes are either complex to operate or require extensive security protocols and are dangerous to conduct. A less complex and hazardous etching process is of interest. In some cases, optical grade semiconductor surfaces are produced by polishing the surface with the aid of chelating agents in the polishing solution [4]. We present a non-hazardous etching method for not time sensitive processes using aqueous solutions of chelating agents at moderate temperatures. Chelating agents are (polydentate) ligands of organic compounds, which form two or more separate coordinate bonds with a single central atom [5]. The aqueous solutions are easy to handle, do not require any special chemical safety precautions, and are low in cost.

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1.1. Hydrofluoric Acid Etching Mechanism of SiN

Based on an analysis by Zambov et al. [6], Knotter et al. [7] determined in a detailed analysis the etching mechanism of HF to be a layer-by-layer process. Amino groups (NH_2) at the surface of the SiN are protonated to ammonia (NH_3^+) by available H^+-ions from the HF solution. Then the Si-N bonds are replaced by Si-F bonds. Finally the SiF_4 is removed from the surface.

1.2. Phosphoric Acid Etching Mechanism of SiN

Phosphoric etching takes place at either moderate temperatures (60°C-90°C) [8] or high temperatures (140°C-200°C) [3]. Both studies suggest a partial hydrolysis reaction, which involves water and phosphoric acid in a reaction. The reaction was modeled by Sundaram et al. [9] to be:

$$3\,\mathrm{SI_3N_4} + 27\,\mathrm{H_2O} + 4\,\mathrm{H_3PO_4} \rightleftharpoons 4\,(\mathrm{NH_4})_3\mathrm{PO_4} + 9\,\mathrm{H_2SiO_3} \tag{1}$$

1.3. Relation of Acidity Constant pKa, pH Value and H^+-Ion Availability

The equilibrium constant for a chemical reaction pKa, for a hypothetical acid HA and its dissociation in water (H_2O) can be shown to have the following relation to the pH value:

$$pH = pK_a + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \tag{2}$$

This equation shows for $\mathrm{pH} - \mathrm{pKa} > 0$ free H^+- ions and A^- are available for the aid of a possible reaction which is also true for solutions of chelating agents [4].

2. Experimental Setup and Measurement

To evaluate the etch rates, different types of SiN are deposited onto different wafers: low stress silicon rich LPCVD silicon nitride (600nm), stoichiometric LPCVD Si_3N_4 (300nm), and low stress PECVD SiN (300nm). The wafers are cut into 1.8mm wide strips. These strips are etched in the experimental setup of round bottom flask with attached condenser. The condenser is necessary due to the long measurement time of up to three weeks. Prior to the experiment the thickness of each strip is determined using a Zeiss interferometer. The pH value of the aqueous solution is determined using a commercial pH measurement system. For the majority of experiments citric acid is used in aqueous solution.

3. Experimental Results

Aqueous solutions of chelating agent etch different SiN. As with other etching methods [9], low stress SiN is etched the slowest, while low stress PECVD SiN is etched the fastest of the three types of thin film SiN (Fig. 1 left).

Solutions with tartaric acid etch SiN faster than citric acid. Using a solution of 20% citric acid we achieve an etch rate of [3.14 ± 0.06] nm/h at 90°C for PECVD grown SiN (Fig. 2 left). Using a solution of 20% tartaric acid an etch rate of [4.38 ± 0.02] nm/h at 80°C for PECVD grown SiN is measured (Fig. 1 left). The etch rate depends on the chelating agent concentration and increases for citric acid from 5% to 25%, above which the etch rate saturates (Fig. 1 right). Surprisingly even deionized water etches SiN. This is related to a hydrolysis reaction [10].

The etching by the chelating agent solution is related to the availability of free H^+-ions. As shown in section 1.3 when the pH value of the solution becomes higher than the pK_a value of the solution the probability of free H+ ions increases. With the increase of H^+-ions the etch rate increases. This is the case for $pH - pK_a > 0$. In Fig. 2 left the change of the acidity constant pKa is shown in relation to a temperature change of 20% citric acid solutions. Once the acidity constant approaches the pH value the etch rates increase. A similar observation can be made for a concentration change of a citric acid solution at a moderate temperature of 80°C (Fig. 2 right). As long as the pH value is larger than the pKa value an etching takes place. The low etch rates for 5% and 10% can be attributed to a competing association reaction with water (from the hydrolysis reaction) and a limited availability of H^+-ions due to the low citric acid concentration. The saturation is a result of the reduced availability of H^+-ions since the pH value decreases below the pKa value at about 35% concentration. Therefore, there is a limit of concentration at which an etch rate is still increasing depending on the temperature applied.

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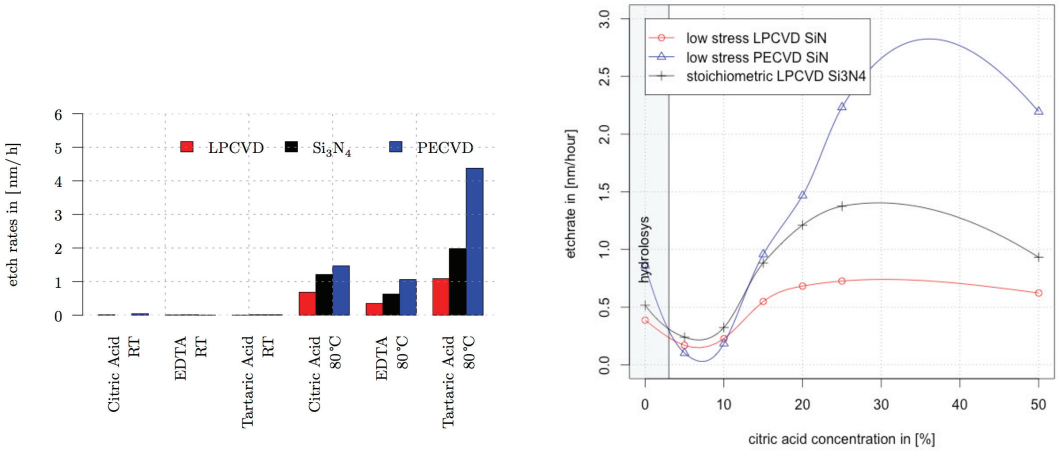

Figure 1 (left) Etch rates for the etching of various silicon nitrides using 20% aqueous solutions of chelating agents at room temperature (RT) and 80°C. Chelating agents shown: citric acid, buffered solution of EDTA, tartaric acid. At room temperature no etching is taking place. At 80°C a significant etching process takes place. Tartaric acid etches the fastest, citric acid etches the slowest.
(right) Silicon nitride etch rates by different dilutions of citric acid at 80 °C. At 0% a hydrolysis takes place. The etch rate increases to a concentration of 25% and then saturates.

4. Conclusion

The involvement of the H+ ions point to a layer-by-layer etching mechanism similar to the HF etching mechanism where N atoms are protonated to ammonia and then removed from the bulk. The needed temperature and the hydrolysis etching show that the Si atoms are removed from the surface in a partial hydrolysis reaction, similar to the etching process of phosphoric acid [8]. Thereforem solutions of chelating agents slowly etch thin layers of Si N with the help of dissociated H^+-ions and a partial hydrolysis at moderate temperatures.

4. Outlook

In order to make the results more applicable for use in semiconductor fabrication future work will analyze sensitivities towards other in MEMS used materials like SiO_2, poly-silicon and the effect on metals. Additionally,m future work will look at possible masking materials and associated information like under etching under possible etching masks.

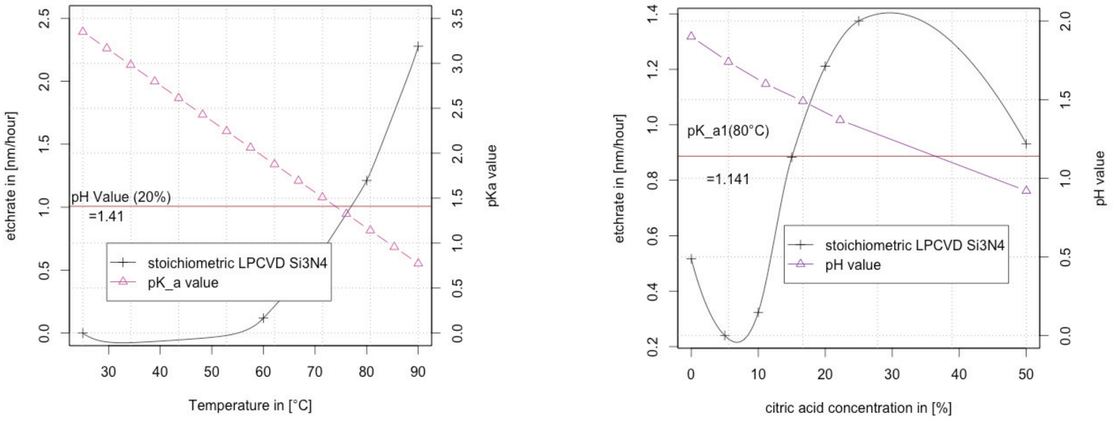

Figure 2: (left) pKa values of citric acid along the etch rates of stoichiometric silicon nitride in aqueous solution of 20% citric acid at different temperatures. For pH >pKa more H+ ions are available which can contribute to an etching reaction.
(right) PH value of different dilutions of citric acid along etch rates of stoichiometric silicon nitride at 80°C. Etching is starting to increase with the presence of free H+ ions due to the imbalance in the acidity: pH > pKa.

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